An ENDOR study of the divacancy in silicon

J G de Wit, C A J Ammerlaan and E G Sieverts
Natuurkundig Laboratorium der Universiteit van Amsterdam, Valckenierstraat 65, Amsterdam, The Netherlands

Abstract. The positive charge state of the divacancy in silicon (Si-G6 EPR spectrum) has been studied by the electron nuclear double resonance method. Hyperfine tensors have been determined for the interaction between the unpaired defect electron and ^{29}Si nuclei ($I = ½$, 4·7% abundant) located at various lattice sites. Hyperfine constants are reported for 18 shells containing a total of 60 lattice sites. The number of lattice sites in each shell is determined by symmetry. There are two possible classes: in the general class each shell contains four equivalent lattice sites. To the mirrorplane class belong those sites which are located in the mirrorplane of the divacancy, each shell containing two equivalent sites. The majority of the tensors are axially symmetric around one of the ⟨111⟩ bond directions of the silicon crystal.

1. Introduction

The divacancy is one of the best understood defects in silicon. It has been studied by electron paramagnetic resonance (Watkins and Corbett 1961, 1965, Ammerlaan and Watkins 1972) and infrared absorption and photoconductivity measurements (Cheng *et al* 1966, Chen and Corelli 1972, Stein 1969). Watkins and Corbett identified two EPR spectra labelled Si-G6 and Si-G7 as arising from the positive and the singly negative charge state of the divacancy. An important feature of these spectra is the hyperfine interaction of the defect electron with magnetic ^{29}Si nuclei located at nearby lattice sites. Using EPR only the largest hyperfine interaction tensor can be determined accurately; hyperfine satellites corresponding to smaller interactions are too close to the central line and are obscured by mutual overlap.

In this paper we report electron nuclear double resonance (ENDOR) measurements on the Si-G6 spectrum associated with the positive charge state of the divacancy. The ENDOR technique developed by Feher (1959) can be used to obtain very accurate measurements of hyperfine parameters for a large number of nuclei. As the hyperfine interaction with a ^{29}Si nucleus at a certain lattice site reflects the local properties of the wavefunction, information about this wavefunction can be obtained by a study of the hyperfine interactions.

Hyperfine parameters were determined by us for 18 shells containing a total of 60 lattice sites. For each shell it can be determined whether the corresponding nucleus is located in the mirrorplane of the divacancy or not. The majority of the tensors are axially symmetric around an axis pointing approximately along one of the ⟨111⟩ bond directions of the silicon lattice.

2. Experimental

Divacancies were produced by 1·5 MeV electron irradiation of 0·1 Ω cm p-type silicon to a fluence of $1{\cdot}8 \times 10^{18}$ electrons/cm^2. A typical sample contained approximately 10^{15} spins. Magnetic resonance measurements were carried out using a superheterodyne spectrometer operating at a frequency of 23 GHz. As the ENDOR signals were quite small (<1% of the EPR signal) the experimental conditions were carefully optimized. Best results were obtained by using a magnetic field modulation at a frequency of 106 Hz and a square wave modulation of the RF field at 3·3 Hz. During measurements the temperature was kept at 17 K. Two different cavity arrangements were used to introduce a RF field at the sample position. Both were TE_{011} cylindrical cavities, one of them using two turns of copper wire as a RF coil (Watkins and Corbett 1964), the other was made of 0·2 mm silver on epibond with a spiral groove cut in such a way that the cavity wall could be used as a RF coil (Woodbury and Ludwig 1960). The samples were approximately cylindrical and had their axis in the $[0\bar{1}1]$ direction. By rotating the magnetic field in the $(0\bar{1}1)$ plane the angular dependence of the ENDOR lines could be determined.

3. Outline of experimental results

3.1. Analysis of spectra

The EPR and ENDOR spectra of the divacancy can be accurately described by a spin Hamiltonian

$$H = \beta \mathbf{H}.\mathbf{g}.\mathbf{S} + \sum_j (\mathbf{S}.\mathbf{A}_j.\mathbf{I}_j - \beta_N g_N \mathbf{H}.\mathbf{I}_j). \tag{1}$$

The first term represents the Zeeman interaction between the electron spin **S** ($S = \frac{1}{2}$) and the magnetic field **H**. The second term is a sum over lattice sites; $\mathbf{I}_j$ is the spin of a ^{29}Si isotope (4·7% abundant, $I = \frac{1}{2}$) at lattice position j. For each lattice site there is a Zeeman term $\beta_N g_N \mathbf{H}.\mathbf{I}_j$ and a hyperfine interaction term. The hyperfine interaction between electron spin **S** and nuclear spin $\mathbf{I}_j$ is characterized by a hyperfine tensor $\mathbf{A}_j$. In its most general form $\mathbf{A}_j$ is a symmetric tensor with three different principal values and three mutually orthogonal principal axes. The number of independent tensor elements is 6.

As the g-tensor of the G6 spectrum is almost isotropic **S** can be taken parallel to **H**. If $\mathbf{I}_j$ is also parallel to **H**, an ENDOR transition is defined by the selection rules $\Delta m_S = 0$, $\Delta m_I = \pm 1$ and the corresponding frequencies are given by

$$h\nu_{\pm} = |\beta_N g_N H \pm \tfrac{1}{2}\mathbf{h}.\mathbf{A}.\mathbf{h}| \tag{2}$$

where **h** is a unit vector along the magnetic field **H** and the ± symbol arises from the two possible spin orientations of the electron.

The effect of the hyperfine interaction on the line position can be described as a hyperfine field $\mathbf{H}_{hf} = \mathbf{A}_j.\mathbf{S}/g_N\beta_N$ which must be added vectorially to the external field **H**. When the anisotropic part of $\mathbf{A}_j$ is small as compared to the Zeeman energy, corrections to equation (2) will not be necessary. This is especially true for the + sign (most of our measurements were taken at the high frequency side of the spectrum).

3.2. Symmetry considerations

A model of the divacancy consistent with the results of EPR studies is shown in figure 1. The defect has the symmetry of the point group $2/m$. Due to this symmetry the lattice sites divide into shells. The atom sites of a shell transform into each other by applying the symmetry operations of the group $2/m$.

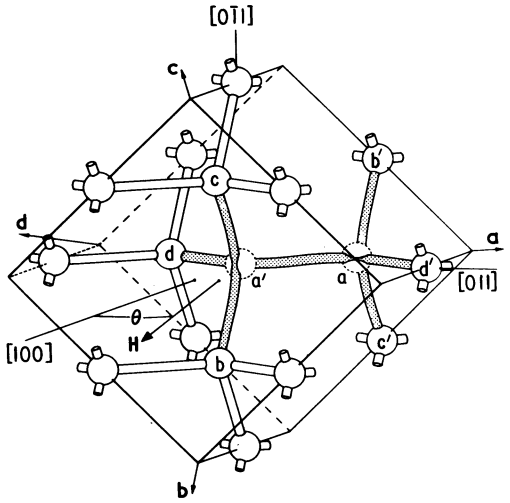

Figure 1. Model of the divacancy in the orientation ad, showing the crystallographic axes. **H** denotes the magnetic field direction as varied in the EPR and ENDOR experiments.

There are two classes of shells: in the general class each shell consists of four equivalent lattice sites; an example of such a shell are the atoms b, c, b′, c′ in figure 1. To the mirrorplane class belong those lattice sites which are located in the mirrorplane of the divacancy; due to the higher symmetry the number of sites in each shell is only two (eg, atoms d and d′ in figure 1).

When the magnetic field is in the (0$\bar{1}$1) plane each shell gives rise to a set of 12 ENDOR lines which can be described by one **A** tensor. Each line corresponds to one of the 12 possible divacancy orientations in the silicon lattice. The reflection symmetry in the case of a mirrorplane class shell causes the ENDOR lines of certain divacancy orientations to coincide; as a result the pattern consists of seven lines. The corresponding **A** tensor has only four independent elements compared to six for a general class tensor.

3.3. Results

Each tensor can be reduced to diagonal form by a coordinate transformation to its principal axes. For a tensor from the general class these principal axes may point in any direction. The largest principal value is taken as A_1, the second largest as A_2. In the case of a mirrorplane class tensor one of the axes has the [0$\bar{1}$1] direction for our basic divacancy orientation ad. Usually this one is called $\mathbf{A}_2$; then $\mathbf{A}_1$ and $\mathbf{A}_3$ are both in the (0$\bar{1}$1) plane, $A_1 > A_3$.

New parameters a, b, c are defined by

$$\mathbf{A} = \begin{pmatrix} A_1 & 0 & 0 \\ 0 & A_2 & 0 \\ 0 & 0 & A_3 \end{pmatrix} \equiv \begin{pmatrix} a+2b & 0 & 0 \\ 0 & a-b+c & 0 \\ 0 & 0 & a-b-c \end{pmatrix}$$

Here $a = \frac{1}{3}\mathrm{Tr}\mathbf{A}$ represents the isotropic part of the hyperfine interaction; it is an important parameter, as its magnitude arises directly from the Fermi contact interaction

$$a_j = \frac{8\pi}{3} \beta\beta_N g g_N |\psi(r_j)|^2. \tag{3}$$

From this relation the square of the electron wavefunction at the jth nucleus $|\psi(r_j)|^2$ can be calculated directly.

The remaining part of the **A** tensor must be ascribed to dipole–dipole interaction. If $c \ll b$ (which is a good approximation for all but three hyperfine tensors) the matrix has axial symmetry and b_j is given by

$$b_j = \tfrac{2}{5}\beta\beta_N g g_N \langle 1/r^3 \rangle_\psi \tag{4}$$

where $\langle 1/r^3 \rangle_\psi$ represents an average over the wavefunction ψ.

In table 1, a, b and c are given for the seven largest interactions in the mirrorplane class and for the 12 largest general class tensors. The direction of the eigenvector associated with each principal value is defined with respect to the mirrorplane of the divacancy ad, the $(0\bar{1}1)$ plane; γ_i is the angle between the ith eigenvector and its projection on the $(0\bar{1}1)$ plane. The angle between this projection and the [011] direction is δ_i. Only γ_1 and δ_1 corresponding to the largest principal value A_1 are given. The seventh column of table 1 gives the approximate direction of $\mathbf{A}_1$. The letters a, b, c and d denote the four $\langle 111 \rangle$ axes: a = $[\bar{1}11]$, b = $[11\bar{1}]$, c = $[1\bar{1}1]$, d = $[\bar{1}\bar{1}\bar{1}]$ (Watkins and Corbett 1965). Of these, a and d are in the symmetry plane of the divacancy orientation ad, b and c are equivalent with respect to reflection in this plane.

4. Discussion

A hyperfine tensor for a certain magnetic nucleus reflects the wavefunction of the defect electron in the immediate neighbourhood of this nucleus. Near the nucleus the potential will be largely atomic in nature. A good choice for a trial wavefunction will therefore be a linear combination of silicon 3s and 3p atomic orbitals centred on various sites neighbouring the divacancy:

$$\psi = \sum_j \eta_j(\alpha_j \psi_{3s} + \beta_j \psi_{3p}). \tag{5}$$

The coefficients α_j, β_j and η_j can be determined easily, knowing that only ψ_{3s} gives a charge density at the nucleus and that contributions to the anisotropic term b_j originate from ψ_{3p} only. Substitution into the formulae (3) and (4) leads to:

$$a_j = \frac{8\pi}{3} g\beta g_N \beta_N \alpha_j^2 \eta_j^2 |\psi_{3s}(0)|^2 \tag{6}$$

Table 1

Nr	*a* (MHz)	*b* (MHz)	*c* (MHz)	γ_1 (deg)	δ_1 (deg)	Axis	α_j^2† (%)	η_j^2 (%)
General class								
G1	22·56	1·95	0·15	4·4	53·1	[211]	22·0	2·49
G2	19·17	0·63	0·58	61·3	−54·6		42·7	1·08
G3	10·24	1·63	0·15	2·5	34·2	d	13·3	1·86
G4	7·08	1·02	0·04	55·6	85·8	b, c	14·5	1·18
G5	3·55	0·35	0·14	47·8	42·1		19·8	0·434
G6	2·145	0·339	0·037	4·1	36·1	d	13·4	0·388
G7	1·778	0·316	0·052	48·5	−87·7	b, c	12·1	0·356
G8	1·608	0·250	0·005	56·5	87·3	b, c	13·6	0·287
G9	1·596	0·245	0·028	11·5	36·9	d	13·8	0·282
G10	0·836	0·093	0·122	51·1	−24·3		18·0	0·112
G11	0·603	0·095	0·014	3·1	60·6		13·8	0·109
G12	0·531	0·082	0·021	1·3	34·8	d	13·8	0·094
Mirrorplane class								
M1‡	148	28		0	34·4	d	11·4	31·3
M2	14·97	2·85	0·240	0	35·3	d	11·4	3·19
M3	5·45	0·90	0·058	0	−27·0	a	12·9	1·02
M4	3·16	0·40	0·055	0	66·7		16·3	0·467
M5	2·53	0·52	0·036	0	30·9	d	10·7	0·572
M6	1·322	0·231	0·010	0	−28·6	a	12·3	0·261
M7	0·977	0·048	0·054	90	–	$[0\bar{1}1]$	33·1	0·071

† $\alpha_j^2 + \beta_j^2 = 1$.
‡ Data taken from Watkins and Corbett (1965).

$$b_j = \tfrac{2}{5} g\beta g_N \beta_N \beta_j^2 \eta_j^2 \langle 1/r^3 \rangle_{3p}. \tag{7}$$

Using the values $|\psi_{3s}(0)|^2 = 31{\cdot}5 \times 10^{24}$ cm^{-3} and $\langle 1/r^3 \rangle_{3p} = 16{\cdot}1 \times 10^{24}$ cm^{-3} as estimated by Watkins and Corbett (1964), α_j^2 and β_j^2 are calculated for each tensor (table 1).

In table 2 a summary of results is given. For a proper set of basis functions the values η_j^2 should add up to 100%. We find a too large value, about 110%, which presumably is due to the non-orthogonality of the atomic orbitals centred on different lattice sites.

In equation (5) ψ_{3p} can be further specified by expansion into $3p_x, 3p_y$ and $3p_z$ orbitals with proper coefficients to yield the experimentally determined direction of the hyperfine axis. A summary of these directions is shown in table 3. Of the 19 hyperfine tensors that are known all but three exhibit approximate axial symmetry. A large

Table 2

	$\Sigma\alpha_j^2\eta_j^2$	$\Sigma\beta_j^2\eta_j^2$	$\Sigma\eta_j^2$
General class	6·8%	28·8%	35·6%
Mirrorplane class	8·6%	65·2%	73·8%
Total	15·4%	94·0%	109·4%

Table 3

Number of tensors	General class	Mirrorplane class
Total	12	7
$A_1 \neq A_2 \neq A_3$	2	1
Approximate axially symmetric $A_1 > A_2 = A_3$	3	1
Approximate ⟨111⟩ axially symmetric	7	5
$A_1 \parallel [\bar{1}11]$ = a	0	2
$A_1 \parallel [11\bar{1}]$ = b or $[1\bar{1}1]$ = c	3	–
$A_1 \parallel [\bar{1}\bar{1}\bar{1}]$ = d	4	3

part of the remaining 16, namely 12, have their axis pointing approximately in one of the ⟨111⟩ directions, which are the bond directions in the silicon crystal. This is reminiscent of sp^3 hybridization. However, inspection of table 1 tells us that for all neighbours, except the nearest ones, on the average α_j^2 equals only 13%.

An enlarged set of atomic orbitals would provide more flexibility in the description of the results. Inclusion of 3d orbitals allows the explanation of deviations from axial symmetry, which is necessary to interpret the G2, G10 and M7 tensors. The effect of core polarization may be considered by including 1s and 2s orbitals in the basis set. A slight difference in the radial dependences of the spin-up and spin-down wavefunctions would have an appreciable effect as the densities of these core wavefunctions are one or two orders of magnitude larger compared to ψ_{3s}. The strongly p-like nature of the defect wavefunction suggests that it may be constructed from states from the upper part of the valence band. The spatially more diffuse character of a wavefunction constructed from Bloch waves is consistent with the present experimental result. The calculations of electronic structures of defects by molecular orbital techniques also show a general agreement with our results. Messmer and Watkins (1972) showed, using extended Hückel theory, that for the vacancy in the diamond lattice about 50% of the electron will be found on the nearest-neighbour sites, while the other half will be appreciably spread out. A similar calculation has been performed for the divacancy in silicon (Lee and McGill 1973). A direct comparison is not possible because detailed information about the wavefunction is lacking in this paper. Assignment of tensors to specific shells will provide a detailed map of the defect electron around the divacancy. However, this matching procedure is a complicated problem usually requiring very detailed calculations (Hale and Mieher 1969, Ivey and Mieher 1972). For the present case molecular orbital theory seems most promising. The ENDOR data will serve as a severe test for any such theory.

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